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Field tests of surface seals and soil treatments to reduce fumigant emissions from shank injection of Telone C35

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ABSTRACT

A mixture of 1,3-dichloropropene (1,3-D) and chloropicrin (CP) (Telone C35) is an increasingly used fumigant product for pre-plant soil fumigation in California, USA. Atmospheric emissions of volatile organic compounds, including these important pesticides, is more heavily regulated in an effort to improve air-quality. Research has identified various methods of reducing fumigant emissions but effective and economically feasible field methods are still needed. The objective of this field study was to determine the effectiveness of several surface seal and soil treatment methods on emissions of 1,3-D and CP from shank-injected Telone C35. Treatments included control (bare surface), pre-irrigation (irrigation prior to fumigation), post-fumigation water seals with or without potassium thiosulfate (KTS) amendment, and standard high density polyethylene (HDPE) tarp over soils amended with either KTS or composted manure. The two KTS treatments resulted in the lowest fumigant emissions; but the soil surface in the treatments developed a reddish-orange color and an unpleasant odor that lasted for a few months. The pre-irrigation reduced emissions more than post-application water seals. An application of composted manure at 12.4 Mg ha^{-1} spread over the soil surface followed by HDPE tarp did not reduce 1,3-D emissions compared to the bare soils in this trial, indicating that a better understanding of processes is required in order to effectively use organic amendments for minimizing fumigant emissions. Chloropicrin emissions were generally lower than 1,3-D for all treatments.

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1. Introduction

Soil fumigation has been an important management practice for control of soil-borne pests for nurseries, orchard replanting, and many annual vegetables. Methyl bromide (MeBr) was used as a broad-spectrum soil fumigant for pre-plant soil fumigation but was phased out due to its effect on stratospheric ozone (Segawa, 2005). Methyl bromide was officially phased out in January 2005 in the U.S. under the provisions of the U.S. Clean Air Act and the Montreal Protocol (an international agreement) (USEPA, 1994) with the exception of MeBr used under critical use exemptions (CUE) or quarantine pre-shipment (QPS) allocations. Alternative fumigants such as 1,3-dichloropropene (1,3-D, Telone), chloropicrin (CP), and metam sodium or metam potassium salt [methyl isothiocyanate (MITC) generators] have been increasingly used in recent years (Cal DPR, 2003; Trout, 2005). These alternative fumigants, however, are volatile organic compounds that react with oxides of nitrogen in the presence of sunlight to form ground-level ozone that is harmful to humans and the environment. Regulations currently in place to minimize the risks of these fumigants in California include specific application

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techniques, timing, and rates designed to reduce emissions, adequate buffer zones, and restrictions on the amount of a product used in a geographical area (Township Caps) (Trout, 2003). More stringent regulations pertaining to the use of soil fumigants are being developed (Cal DPR, 2007a,b).

Research and practice have identified various surface seals or treatment methods to minimize emissions, such as various plastic tarps, water seals, and soil amendments with chemicals such as ammonium or potassium thiosulfate (ATS or KTS) and organic materials (Yates et al., 2002). Effective use of plastic tarps to minimize emissions largely depends on the tarp permeability to the specific fumigant and the ability of the tarp to retain those permeability properties after installation under field conditions (Ajwa et al., 2007; Qin et al., 2008). Field tests showed that post-fumigation water seals could effectively reduce emissions of MITC (Sullivan et al., 2004), 1,3-D, and CP (Gao and Trout, 2007). Soil amendment with chemicals, such as thiosulfate or thiourea can transform fumigants to non-volatile compounds and effectively reduce fumigant emissions (e.g., Gan et al., 1998a; Wang et al., 2000; Zheng et al., 2006, 2007; Qin et al., 2007). Amendment of soils with organic materials such as composted manure can increase fumigant adsorption and enhance degradation of fumigants in soils to reduce emissions (e.g., Gan et al., 1998b; Kim et al., 2003; Dungan et al., 2001, 2005; Ashworth and Yates, 2007; McDonald et al., 2008).

Most tests on soil amendment with chemical or organic material have been conducted in soil column experiments and some small field tests. Tests under field conditions are necessary to define effective, economically feasible, and environmentally safe methods to minimize fumigant emissions. This research was designed to compare several potential surface seal and soil treatment methods to reduce emissions from soil fumigation. The specific objective was to determine the effectiveness of surface seal (tarp or water) and soil treatments (irrigation and amendment with chemical and composted manure), as well as combination methods, to reduce emissions of 1,3-D and CP from broadcast applications of Telone C35 under field conditions.

2. Materials and methods

A field trial was conducted from Oct. 17–31, 2006 at the USDA-ARS San Joaquin Valley Agricultural Sciences Center, Parlier, CA (Latitude: 36° 35′ 36.74″ N; Longitude: 119° 30′ 48.71″ W). The soil was a Hanford sandy loam (coarse-loamy, mixed, superactive, non-acid, thermic Typic Xerorthents) and properties of the soil were reported in earlier studies (Gao and Trout, 2007). During the field trial, the daily maximum and minimum air temperature were in the range of 20–30 and 2–9 °C, respectively.

2.1. *Soil preparation, fumigation and treatments*

A field strip (150 m long and 9 m wide) was prepared for fumigation by cultivating to 76 cm depth. Because the surface 15 cm soil was dry, the field was pre-irrigated with sprinklers two weeks prior to fumigation. Irrigation was stopped when the wetting front reached about 8 cm depth. The soil profile moisture condition for top 50 cm soil prior to fumigation averaged 8% (v/v or 5.1%, w/w), which was 30% of field capacity (17%, w/w) on the day before fumigation.

Half of the field strip (150 m long and 4.5 m wide) was fumigated by shank injection of Telone C35 to a depth of 45 cm below soil surface. The other half was not fumigated, serving as a comparison to the fumigated area for efficacy studies (Hanson et al., 2007). The fumigation was applied by a commercial fumigant applicator (TriCal Inc., Holister, CA) on Oct. 17, 2006 using a rig with 8 shanks spaced 50 cm apart. Fumigation started at 0900 h and was completed within 5 min in one pass across the field. The total amount of Telone C35 applied was 500 kg ha^{-1} (445 lb ac^{-1}). Immediately following fumigation, the field surface was tilled by a spring tooth harrow and ring roller in a one pass operation to compact the surface soil and eliminate large pores and shank traces.

Six surface seal or soil treatments were tested with three replicates in a randomized complete block design. A 3-m wide buffer zone was left between blocks and treatments with water applications. Treatment plot size was 9 m×3 m (tarped treatments) or 9 m×9 m (irrigation treatments). These treatments included irrigation prior to fumigation, water seals after fumigation, and amendment of surface soils with potassium thiosulfate (KTS) with or without HDPE tarp or composted steer manure with HDPE tarp. These treatments had shown potential in reducing fumigant emissions in previous research either in soil columns or small field plot tests (e.g., Gan et al., 1998a,b; Zheng et al., 2006; Gao and Trout, 2007). One of the main purposes of this field trial was to test these treatments simultaneously under field conditions for their effectiveness in controlling emissions as well as efficacy for controlling soil pests. Pest control results are given by Hanson et al. (2007). Treatments are summarized below:

1. Control (bare soil without irrigation or tarping).
2. Manure + HDPE (manure application rate was 12.4 Mg ha^{-1}).
3. KTS + HDPE (KTS was applied in 4 mm water at 1000 kg ha^{-1} (a.i.) or 2:1 KTS/fumigant mass ratio, which was equivalent to 1.4:1 molar ratio).
4. Pre-irrigation (34 mm water was applied 4 days prior to fumigation).
5. Intermittent water seals (13 mm water was applied immediately following fumigation, with additional 4 mm water applications at 12 h, 24 h, and 48 h).
6. Intermittent KTS applications (KTS at 1000 kg ha^{-1} (a.i.) or 2:1 KTS/fumigant ratio immediately following fumigation, and at 500 kg ha^{-1} (a.i.) or 1:1 ratio at 12, 24, and 48 h using the same amount of water as treatment #5).

For treatment 2 (manure + HDPE), composted steer manure purchased from a local garden center was spread over the soil surface immediately after fumigation and surface preparation but before tarping. The organic materials were not incorporated into the soil. The manure application rate of 12.4 metric tons per acre is a common fertilizer rate used by many growers in the region. Higher application rates of manure would require higher costs and feasibility should be determined. Within 30 min of fumigation, the manure was applied and the HDPE tarp was installed using commercial fumigation equipment (Noble plow rig).

For treatment 3 (KTS + HDPE), KTS® was obtained in the 50% liquid formula (KTS, 0-0-25-17S) from Tessenderlo Kerley (Phoenix, AZ), and was applied in 4 mm water using a 3 m wide spray bar. The HDPE tarp was hand-applied to avoid the compaction of wet surface soils after application of KTS solution.

For treatment 4 (pre-irrigation), 34 mm water was applied four days prior to fumigation using a sprinkler-irrigation system with one sprinkler at each corner of each 9 m×9 m plot. This amount of water was expected to result in a soil water content (SWC) of 60% of FC for the top 30 cm of soil.

For treatment 5 (intermittent water seals), the water seal was applied to each plot using the sprinkler-irrigation system described above. Thirteen mm of water was initially applied following fumigation to moisten the top 8 cm of soil. Application of this amount of water took about 1.5 h following fumigation. For subsequent water applications at 12, 24, and 48 h, 4 mm of water was applied in about 25 min.

For treatment 6 (intermittent KTS applications), the application schedule and the amount of water used in delivering KTS to soil surface were the same as treatment 5. At the initial application following fumigation, the KTS solution at a 2:1 KTS/fumigant (w/w) ratio was applied in the last 30 min of sprinkler irrigation. For the subsequent application, i.e., at 12, 24 and 48 h, a 2:1 KTS solution was applied in 4 mm water.

2.2. *Sampling and measurement*

Sampling for air emissions and soil soil-gas distribution of applied fumigants (1,3-D and CP) was conducted for two weeks following fumigation. At the end of the sampling period, soil samples were collected for residual fumigants in the soil. Soil water content was determined for the control and pre-irrigated plots on the day before fumigation, 4 days later, and at the end of the field trial for all plots. Soil temperature at 10-cm depth was measured for one day during the trial.

Air emission sampling, sample processing and analysis followed procedures previously reported in Gao and Trout (2007) with minor modifications indicated below. Briefly, emissions were measured using static (passive) flux chambers. The chambers were placed on the soil surface or tarp for 15 min and then a 100-mL gas sample was withdrawn from inside the chamber using a gas-tight syringe through a sampling port at a flow rate ~100–200 mL min^{-1}, and through an ORBO™ 613, XAD 4 80/40 mg (Supelco, Bellefonte, PA) sampling tube for trapping both 1,3-D and CP. The sampling tubes were immediately capped, stored on dry ice in the field, and transferred into an ultra-freezer (– 80 °C) in the laboratory. The fumigants were extracted from the tubes and analyzed within 4 weeks using a gas chromatograph with a micro electron capture detector (GC-μECD). Storage of the sample extracts did not result in significant loss of fumigants. Based on analysis of 130 samples before and after storage of one month, relative standard deviations were 2.2 (±4.6), 1.8 (±4.9), and 1.5 (±10.6) for *cis* 1,3-D, *trans* 1,3-D, and CP, respectively. Emission sampling was done every 3 h for the first 48 h and every 4 h thereafter during the day. No sampling was done at night (1700 to 0800 h) after the first two nights. Average flux or emission rates were calculated during the 15-min capture time based on fumigant concentration measured and soil surface area covered. Cumulative emissions of 1,3-D (sum of *cis*- and *trans*-1,3-D isomers) and CP were estimated by summing the products of the average of two consecutive emission flux values and the time interval between the two measurements over the time span of the study.

Fumigant concentration in the soil-gas phase were sampled using stainless steel sample probes installed to 10, 30, 50, 70, and 90 cm below the soil surface. A 50-mL soil-gas sample was withdrawn through an ORBO613, XAD 4 80/40 mg tube using a gas-tight syringe. Measurements were done at two locations (a, adjacent to shank line; b, between shank lines) in one replicate of the treatments at 6, 12, 24, 36, 48, 72, 120, 168, 240, and 312 h following fumigation. Processing of the soil-gas sampling tubes was the same as the emission samples.

At the end of the field trial, soil samples were taken at 20-cm depth intervals to 100 cm to determine residual fumigants in the soil. Samples were collected with a bucket auger, mixed immediately and a portion placed in a screw-top glass jar that was stored on dry ice in the field, and in a freezer (– 80 °C) in the laboratory until extractions. The samples were extracted with ethyl acetate and analyzed using a GC-μECD system using the procedure reported in Gao and Trout (2007).

2.3. *Statistics*

For statistical analysis, SAS OnlineDoc® 9.1.2 (SAS Institute Inc., 2004) was used to analyze the significance of treatment effects on total fumigant emissions. Because of the randomized complete block design, a two-way factorial analysis of variance (ANOVA) was employed and the means were separated using Tukey's HSD (honestly significant difference) test.

3. Results and discussions

3.1. *Emission flux*

Fig. 1 shows emission flux for both 1,3-D and CP from the six treatments. The control gave the earliest and longest duration (24 h) peak emissions (25 μg m^{-2} s^{-1} for 1,3-D and 15 μg m^{-2} s^{-1} for CP). The 1,3-D and CP emission peaks in this experiment, however, were much lower than in previous field tests conducted on similar soils with lower soil water content (Gao and Trout, 2007; Gao et al., 2008). In a field trial conducted in summer (max. daily air temperature: 37–41 °C), the measured peak emission rate was 75 μg m^{-2} s^{-1} for 1,3-D from a control with a soil water content of 3% for top 30 cm soil (Gao and Trout, 2007). In another trial conducted during a period of lower temperatures (max. daily air temperature: 13–27 °C), a control with similar dry surface soil (water content: ~3%) gave a similar peak emission of 76 μg m^{-2} s^{-1} for 1,3-D and 53 μg m^{-2} s^{-1} for CP (Gao et al., 2008). In the current field trial conducted under fall weather (max. daily temperature: 20– 30 °C), the field was more moist than the two previous trials with an average soil water content of 8% (30% of FC) for top 30 cm soil. This difference in soil water content may have contributed to the lower emissions in this field trial indicating the important influence of soil moisture on fumigant peak emission flux.

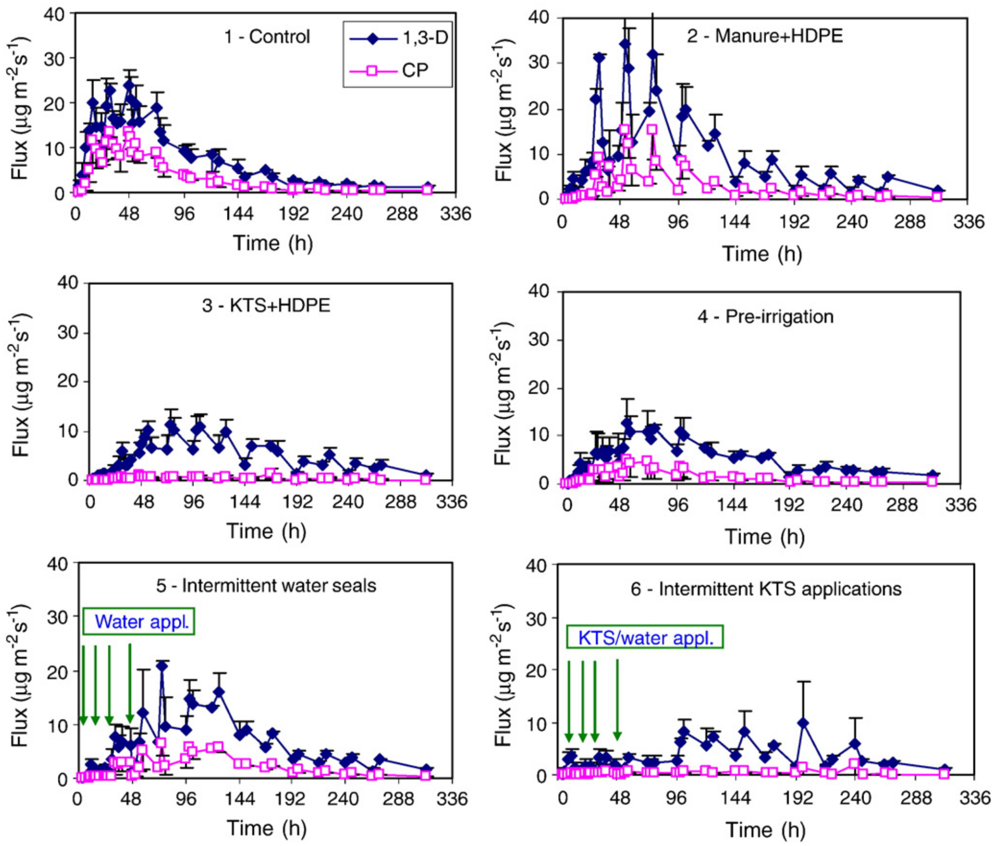

Fig. 1 – Effects of surface seal and soil treatments on emission flux of 1,3-dichloropropene (1,3-D) and chloropicrin (CP) from shank injection of Telone C35. Error bars are standard deviations of the mean (*n*=3). Manure, composted steer manure; HDPE, high density polyethylene; KTS, potassium thiosulfate.

The amendment of manure plus HDPE tarp unexpectedly gave higher 1,3-D peak emission rates than the control (Fig. 1) during the daytime possibly due to higher daytime soil temperatures under the tarp than bare soil (Fig. 2). This may be due to reduced affinity of the fumigant for organic materials when the temperature was high or possibly because the composted manure was not incorporated into the soil that was unable to react effectively with fumigants. Similar results were observed from a soil column test in which composted manure spread over the soil surface gave much higher 1,3-D emissions (unpublished data) than when incorporated into surface soil (McDonald et al., 2008). These results indicate that incorporation of organics into surface soils may be necessary to reduce emissions.

The KTS plus HDPE tarp greatly reduced fumigant emission rates especially for CP. For 1,3-D, both the KTS + HDPE tarp and the pre-irrigation treatments resulted in similar low emission rates. The post-fumigation intermittent water seals resulted in low emissions for the first 48 h but emissions at later times (48–192 h) were as high as the control. When KTS was applied with water seals (intermittent KTS application treatment), emission rates were low for four days for 1,3-D and through the whole experimental period for CP. The results indicated that KTS is very effective for reducing emission rates, especially for CP.

The KTS worked much more efficiently than manure to reduce fumigant emissions. KTS reacts rapidly with halogenated fumigants to form non-volatile compounds (Gan et al., 1998a). Manure, degrades fumigants both biologically by enhancing microbial activity and chemically (Dungan et al., 2001, 2003; Gan et al., 1998b) and may also involve some reversible sorption processes as indicated by Kim et al. (2003).

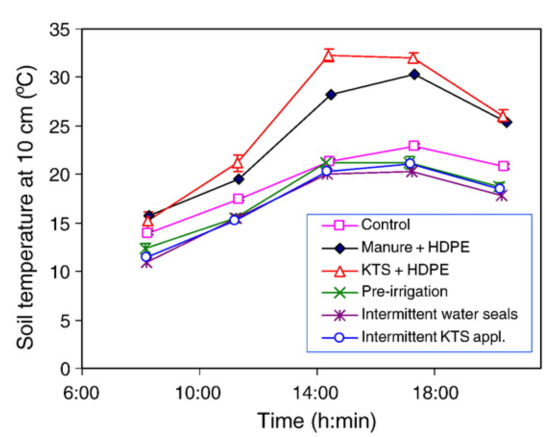

Fig. 2 – One-day soil temperature measurements at 10-cm soil depth during fumigant emission monitoring period. Horizontal bars are the standard deviations of the mean (*n*=3). Manure, composted steer manure; HDPE, high density polyethylene; KTS, potassium thiosulfate.

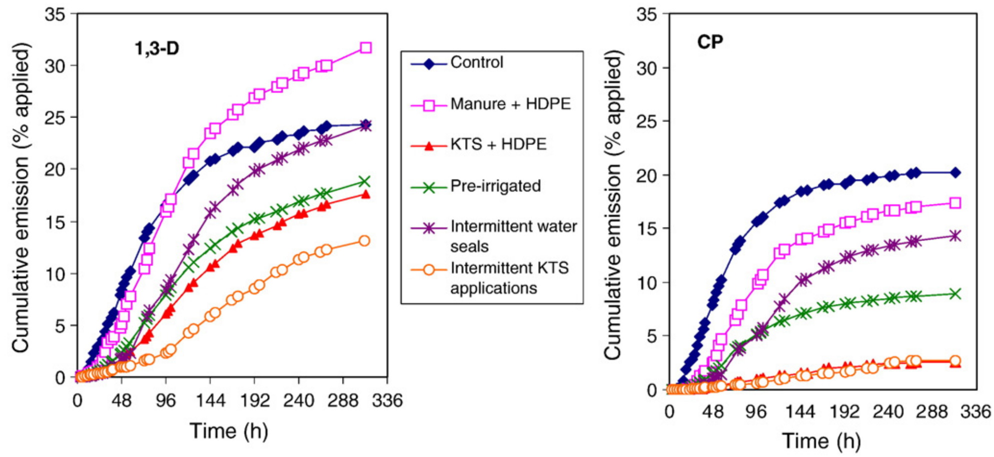

Fig. 3 – Cumulative emission losses of 1,3dichloropropene (1,3-D) and chloropicrin (CP) from surface seal and soil treatments. Plotted data are averages of three replicates. Manure, composted steer manure; HDPE, high density polyethylene; KTS, potassium thiosulfate.

Fumigant emission rates showed a diurnal pattern, which was greater for the manure plus HDPE tarp treatment than others. The tarps increased daytime soil temperature compared to bare soils (Fig. 2). Partitioning of fumigants into the soil-gas phase and fumigant desorption from the soil solid/liquid phases increases with temperature. Also, the tarp permeability increases with temperature (Papiernik and Yates, 2002). The unincorporated composted manure materials were unlikely able to react with fumigants effectively as discussed above. All these factors may have resulted in the higher emission rates, especially during the day time. Most studies have showed that incorporation of organic materials effectively reduced fumigant emission when the organics were incorporated into soil or when studies were conducted in soils with high organic matter (e.g. Dungan et al., 2001, 2005; Ashworth and Yates, 2007; McDonald et al., 2008). Kim et al. (2003) reported increased adsorption of 1,3-D with soil organic mater. Most previous studies used much higher organic application rates than this study, up to 5% (w/w, or equivalent to 60 Mg ha^{-1}). The lower amount of manure used in this study may have also contributed to the lack of emissions reductions. Better understanding of the interaction between organic matter and fumigants under field conditions is needed in order to reliably reduce emissions from soil fumigation using organic amendments.

The effect of organic matter on phase partition of 1,3-D isomers was studied in detail by Kim et al. (2003). At 20 °C, the partitioning coefficient K_H between air and water (concentration in air/concentration in water at equilibrium) for *cis*- and *trans*-1,3-D were 0.052 and 0.033, respectively. The partitioning between soil and water were was described by K_f (Freundlich adsorption coefficient) and ranged from 0.47 to 0.60 for *cis*-1,3-D and 0.39 to 0.45 for *trans*-1,3-D, respectively for soils with no amendments. These values (less than 1) implied that 1,3-D was very weakly adsorbed on soils. However, for a muck soil with much higher soil organic matter content and manure compost, the K_f values increased to 8.55 for *cis*-1,3-D and 6.96 for *trans*-1,3-D, respectively. These results indicate the important role of organic matter for enhancing fumigant adsorption. Further, in their study, a soil in which organic matter was removed using H_2O_2-oxidation showed about 50% reduced fumigant adsorption. Stronger hysteresis in fumigant desorption was also observed for soil with higher organic matter content. The incorporation of fumigants into organic phase was also reported by Xu et al. (2003) who found that incorporation of 1,3-D to soil humic substances followed the order of fulvic acids>>humin>humic acids. Although the affinity of fumigants to organic matter is much higher than to soils, its role in fumigant dissipation in soils may be limited because most soils in which fumigation used have low organic matter content. For effective emission reductions, amendments with high amounts of organics may be needed.

3.2. *Cumulative emission losses*

The cumulative and total emission losses of 1,3-D and CP as a percent of applied over a 2-wk monitoring period are shown in Fig. 3 and Table 1. The control treatment resulted in the earliest and highest 1,3-D emission losses in the first few days, but was exceeded by the manure + HDPE tarp treatment after 96 h (Fig. 3). Chloropicrin emissions in the manure + HDPE tarp

Table 1 – Total emission loss of 1,3-dichloropropene (1,3-D) and chloropicrin (CP) measured over 2 weeks after fumigation

Treatment[a]	Total emissions (% of applied)[b]	
	1,3-D	CP
Control	24 (a, b)	20 (a)
Manure+HDPE	32 (a)	17 (a, b)
KTS+HDPE	18 (b)	3 (b)
Pre-irrigation	19 (b)	9 (a, b)
Intermittent water seal	24 (a, b)	14 (a, b)
Intermittent KTS appl.	13 (b)	3 (b)

[a] Manure, composted steer manure; HDPE, high density polyethylene; KTS, potassium thiosulfate.
[b] Within a column, means (n=3) with the same letter in parentheses are not significantly different according to Tukey's HSD test (α=0.05).

treatment continued to be lower than the control (Table 1). The KTS + HDPE tarp treatment resulted in much lower cumulative emissions, especially for CP. The intermittent water seals did not reduce total 1,3-D or CP emissions compared to the control. Intermittent KTS applications resulted in the lowest measured emissions for both 1,3-D and CP. The pre-irrigation treatment from this field test resulted in the second lowest cumulative emissions. Statistical analysis of cumulative emissions indicated that 1,3-D emissions did not differ significantly between the control and any other treatment; however, manure + HDPE had significantly higher emissions than the pre-irrigation and both KTS treatments (Table 1). Chloropicrin emissions for both KTS treatments were significantly lower than the control treatment. Although the within-treatment variability of these data made statistical separations difficult, the absolute differences among some treatments suggest that soil moisture management can reduce total fumigant emissions.

The KTS applications most effectively reduced emissions in this trial. However, surface soils from all KTS treatments showed distinct reddish-orange color accompanied by a strong and unpleasant odor. This odor and color lasted for a couple of months and slowly diminished during the winter rainy season. The color change in this soil only occurred in the fumigated areas and was not observed in the non-fumigated areas with KTS applications. Zheng et al. (2007) recently reported that volatile 1,3-D can react with thiosulfate to generate a non-volatile Bunte salt via a chemical reaction. Although this derivative was relatively stable at neutral and moderately acidic aqueous solutions, several volatile/semivolatile organic sulfur products were detected in soils treated with the thiosulfate derivative of 1,3-D. These sulfur compounds were produced through biological process and suspected to be the source of the strong odor. The fate of these compounds and environmental impacts are still not clear. From our field test results, the soil color change from KTS application to fumigated soils indicates soil chemical reactions that are not fully understood. These reactions should be better understood before recommending KTS use for fumigant emission reduction.

Pre-irrigation has a practical and economic advantage among all the emission reduction treatments due to its easy application. The effectiveness of this treatment was shown in two previous trials (Gao and Trout, 2007; Gao et al., 2008) when irrigation was applied 2 to 4 days prior to fumigation with a water amount that tended to wet the surface 25–30 cm soil to field capacity. An irrigation applied four days before fumigation in October resulted in emission reductions of about 50% for 1,3-D and 70% for CP compared to bare soil (Gao et al., 2008). A pre-irrigation plus HDPE tarp in a summer trial showed similar emission reductions as an intermittent water seal treatment (Gao and Trout, 2007). In the current study, pre-irrigation reduced cumulative emissions more effectively than the intermittent water seals, which gave higher emissions after four days than the pre-irrigation treatment for both 1,3-D and CP (Fig. 3). There was no difference in 1,3-D total emission losses by the end of the trial from the intermittent water seals compared to the control. The results indicate that proper irrigation management prior to fumigation can reduce cumulative emissions as effective as post-fumigation water seals. It is critical, however, that the amount of water should not be excessive which may significantly reduce fumigant distribution through the soil or fumigant concentrations in soil-gas phase and lead to reduced efficacy (McKenry and Thomason, 1974; Thomas et al., 2003). It is important to monitor fumigant distribution and/or measure fumigant efficacy when evaluating emission reduction methods.

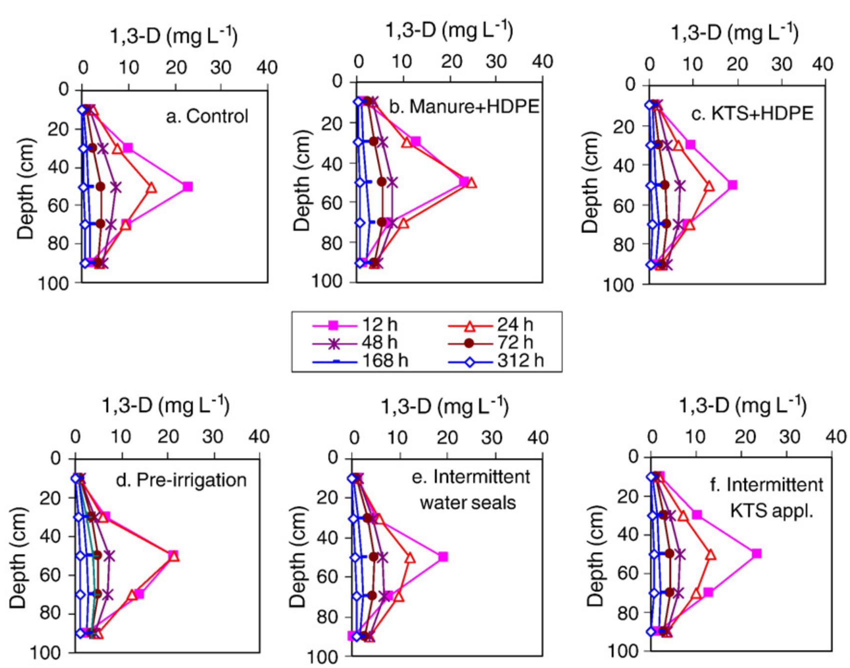

Fig. 4 – 1,3-dichloropropene (1,3-D) distribution in soil-gas phase under various surface treatments at location *a* — adjacent to fumigant injection lines. Manure, composted steer manure; HDPE, high density polyethylene; KTS, potassium thiosulfate.

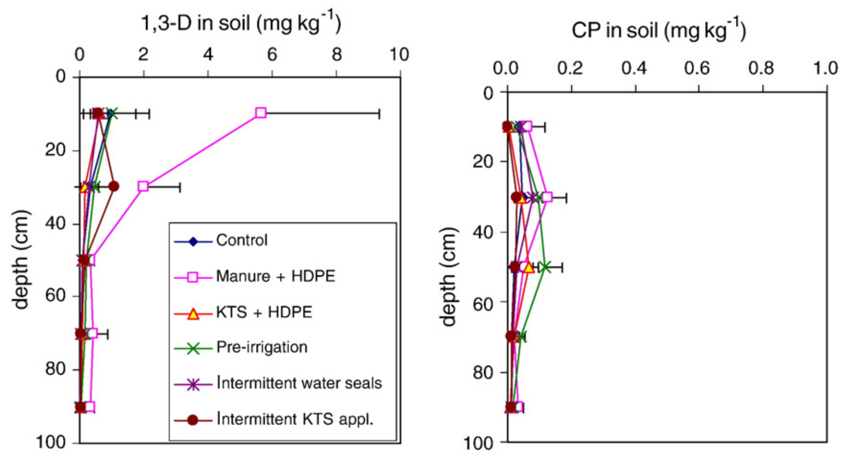

Fig. 5 – Residual 1,3-dichloropropene (1,3-D) and chloropicrin (CP) extracted from soil samples 14 days after fumigation. Error bars are standard deviations of the mean (*n*=3). Manure, composted steer manure; HDPE, high density polyethylene; KTS, potassium thiosulfate.

3.3. *Fumigants in soil air*

Fumigant concentration in the soil-gas phase monitored over time following fumigation is given in Fig. 4 at sampling location *a* (on the shank shank-injection line). Distribution patterns of CP (data not shown) were similar to 1,3-D with generally lower concentrations than that of 1,3-D. Higher fumigant concentrations were usually observed at location *a* compared to between shank-injection lines (location *b*, data not shown) especially at earlier sampling times. The highest fumigant concentration observed for each treatment was near injection depth (50 cm) at 6 or 12 h following fumigation for location *a* and usually 12 or 24 h for location *b*. This reflects the time required for distribution of fumigants through the soil and these differences decreased with time. The maximum fumigant concentrations at 12 h ranged from 19 to 23 mg L^{-1} for location *a* and from 9 to 14 mg L^{-1} for location *b*. At 48 h, continuing redistribution resulted in a much narrower range in the maximum fumigant concentrations among the treatments in soil profile and between locations (6.6 to 7.7 mg L^{-1} for location *a* and 5.6 to 7.3 mg L^{-1} for location *b*).

Comparison between treatments showed that relatively higher soil-gas concentrations were measured in the treatment of manure + HDPE at most times. The manure amendment most likely increased fumigant adsorption as discussed above. The increased soil water content in the pre-irrigated plots could reduce fumigant diffusion to the surface and reduced emissions. This treatment, however, did not appear to inhibit fumigant distribution in this soil as similar concentration and distribution were observed as in other treatments as well as between locations *a* and *b*. The lowest fumigant concentrations in soil air were observed from KTS + HDPE tarp with larger differences from other treatments at location *b*. Data from the last sampling (2 weeks after fumigant injection) indicate that small amounts of the fumigants were still detected (up to 1.2 mg L^{-1} 1,3-D and 0.7 mg L^{-1}CP) with all the treatments.

3.4. *Residual fumigant*

Residual 1,3-D and CP extracted from soil samples (fumigants contained in the solid/liquid phase) taken 14 days after fumigation are shown in Fig. 5. Concentrations of 1,3-D were higher in upper soil layers than those below. Concentrations of CP were much lower (mostly below 0.2 mg kg^{-1}) than 1,3-D. For 1,3-D, only manure-incorporated surface soils had an average of 1,3-D concentrations above 2 mg kg^{-1} with a large standard deviation. The results were supported by Kim et al. (2003), whose study showed that adsorption of 1,3-D in native soils and soils amended with manure compost increased with increasing soil organic matter content. The higher amounts of residual fumigant in the manure amended soils partially explain the high emission rates during the daytime when high temperatures may have caused desorption of fumigants from solid/liquid phase and partitioning to soil-gas phase.

3.5. *Soil water content*

Fig. 6 illustrates the effect of pre-irrigation on soil water content. The pre-irrigation treatment which was applied 4 days prior to fumigation increased soil water content to

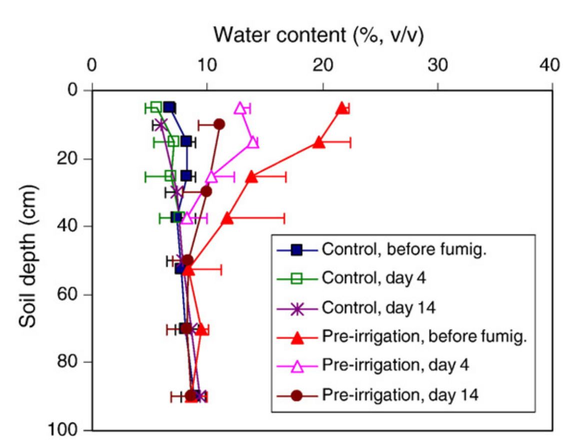

Fig. 6 – Soil water content measured the day before fumigation and 4 and 14 days after fumigation under various surface treatments. Error bars are the standard deviations of the mean (*n*=3).

40 cm depth compared to the non-irrigated treatments. The whole field had been irrigated two weeks prior to fumigation and the control had a fairly uniform soil water distribution by the day before fumigation (8%, v/v) which is about 30% of the field capacity. The pre-irrigated soil had much higher soil water content at soil surface on the day before fumigation (21% v/v or about 80% of FC). The soil water content decreased with depth and with time. By the end of the field trial (2 weeks later), the soil water content for the pre-irrigation was about 35–40% of FC. As indicated above, the pre-irrigation did not reduce fumigant concentration in the soil-gas phase compared to the control and other treatments (Fig. 4) but effectively reduced emissions. To take best advantage of irrigation in reducing emissions, fumigation should be applied within a few days after an irrigation or as soon as soil conditions allow. Irrigation water mostly remains near the surface soil and the higher surface soil water content forms an effective surface barrier to emissions.

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